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SEPARATIONS

Hydrogen Transport through Tubular Membranes of Palladium-Coated Tantalum and Niobium

Robert E. Buxbaum* and Andrew B. Kinney

Chemical Engineering Department, Michigan State University, East Lansing, Michigan 48824, and REB Research & Consulting, 25451 Gardner, Oak Park, Michigan 48237

Palladium-based membranes have been used for decades in hydrogen extraction because of their high permeability and good surface properties and because palladium, like all metals, is 100% selective for hydrogen transport. We describe experiments with hydrogen-extraction membranes made of palladium-coated niobium and tantalum heat-exchanger tubes. The cost was about \$45/ft of $\frac{3}{8}$ in. tubular membrane, and the fluxes were as high as $0.00147 \text{ mol/m}^2 \text{ s Pa}^{1/2}$ at 420°C . The main transport resistance is in the refractory metal substrate. Durability tests showed a 15% reduction in flux for 31 days of continuous membrane operation. Assuming durability is maintained for at least 1 year, this price and flux should allow competitive application for hydrogen recovery in petrochemical plants and for membrane reactors.

Introduction

Palladium membranes have been used for decades to provide very pure hydrogen for semiconductor manufacture, fuel cells, and laboratory use. Palladium combines excellent hydrogen transport and discrimination properties with resistance to high temperatures, corrosion, and solvents. Further, palladium is easily formed into tubes that are easily fabricated into hydrogen extraction units^{1,2} and palladium surfaces are not readily poisoned by carbon monoxide, steam, and hydrocarbons.^{1,3,27} These properties would make palladium membranes very attractive for use with petrochemical gases except that palladium and its alloys are expensive and soft. Membrane units must employ thick-walled tubes costing \$3000/ft² or more. Further, the thick wall lowers the hydrogen flux since flux is inversely proportional to membrane thickness. Thus, despite their advantages, palladium-alloy membranes are usually too expensive for large-scale hydrogen recovery and membrane reactors.

Developmental History of Composite Metal Membranes

As Figure 1 shows, several low-cost refractory metals have greater hydrogen permeabilities than palladium. These metals, including niobium, tantalum, and vanadium, are also stronger than palladium and are easily fabricated into tubes and other useful shapes. Thin-walled tubes of these metals would show very high hydrogen fluxes at a fraction of the cost of palladium, but until recently their poor surface properties reduced transport dramatically.⁴⁻¹³

In 1967, Makrides et al. at Harvard University⁴ patented a hydrogen-extraction membrane where a refractory metal was coated with palladium to facilitate hydrogen ingress and egress and to prevent oxidation of the refractory metal surfaces. The resulting mem-

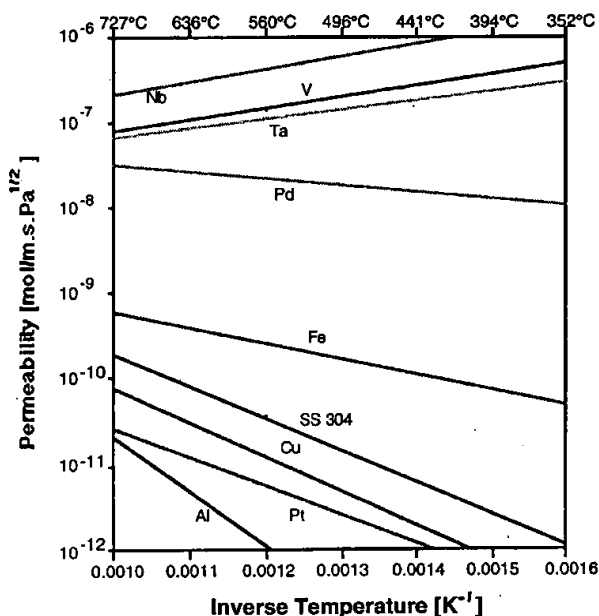


Figure 1. Hydrogen permeabilities of selected metals.

brane showed greater hydrogen transport than with palladium or its alloys, was strong, produced 100% pure hydrogen, and had a high tolerance to pinhole defects in the coat. Although the coat was not continuous, selectivity remained 100% because the nonporous substrate blocked non-hydrogen gas transport that penetrated defects in the coat.

Makrides et al.'s membranes achieved limited application though because the coating process, palladium vapor deposition at high vacuum, was expensive and deficient. Vapor deposition does not coat inside tubes, the preferred extractor configuration, and generally retains significant surface transport resistance. Hydrogen transport, while higher than with palladium, was one-tenth that predicted from the data in Figure 1. Makrides et al.'s vapor-coated membranes found use only in the nuclear industry where the high cost is offset

* Author to whom correspondence is addressed. Phone: 810-547-7942. home page <http://www.tcimet.net/reb/buxt.htm>.

by the membranes' high flux and durability. A palladium-coated alloy membrane worked for over 10 000 h continuously, removing hydrogen from metal-cooled nuclear reactor fluids,⁹ and palladium-coated zirconium has been tested successfully for removing embrittling deuterium from CANDU reactor bundles.¹⁴

More recently, Hsu and Buxbaum patented a lower-cost electroless deposition process for applying a uniform palladium coat to refractory metals, even inside tubes.¹⁵ Amano et al.¹⁹ demonstrated membranes of a non-embrittling vanadium alloy which extends the range of coated-membrane operation, in theory, down to room temperature. Also, flux measurements with coated tantalum, niobium, and zirconium disks have generally corroborated the predictions in Figure 1 and corroborated the predicted 100% hydrogen selectivity.^{10,16} The permeance of a 0.25 mm wall niobium tube at 420 °C was found to be 0.0007 mol/m² s Pa^{1/2}, much higher than that for a Ube polymer membrane operating at 100 °C and these pressure drops.¹⁶ However, the predicted cost was \$500/ft², more than double that for polymeric membranes.³¹

Background to Hydrogen Transport in Metals

Hydrogen transport through metals has been studied extensively.^{11,13,17,18} Since hydrogen molecules dissociate into atoms to diffuse through metals, transport is calculated from the atomic flux. Fick's first law describes the flux of hydrogen atoms through a homogeneous phase as:

$$N_H + \delta D_M (\sim C_H / \delta_M) \quad (1)$$

where N_H is the atomic flux, D_M is diffusivity, $\sim C_H$ is the change in hydrogen atom concentration across the membrane, and δ_M is the membrane thickness. C_H is related to the partial pressure of hydrogen in equilibrium with the metal, correlated for example by

$$C_H + K_S (P^{1/2}) \quad (2)$$

where K_S is the Sieverts constant and P is the partial pressure of hydrogen in equilibrium with the metal. The power of $1/2$ comes from the dissociation of hydrogen molecules into twice as many atoms at low concentration.

We now calculate the flux of hydrogen molecules, N , in terms of pressure using eq 1 and 2. Since the flux of molecules is half the flux of atoms:

$$N + (D_M K_S / 2 \delta_M) \sim P^{1/2} + \Theta_M \sim P^{1/2} / \delta_M \quad (3)$$

The term Θ_M above is called the metal permeability,

$$\Theta_M + D_M K_S / 2 \quad (4)$$

a pressure-independent constant for a given metal at low hydrogen contents. Two derived quantities, the "permeance" and the "total resistance to transport", are respectively the flux divided by the pressure driving force and the inverse of this number. These numbers are related to the average permeability, $\bar{\Theta}$.

$$\text{permeance} \equiv N / \sim P^{1/2} + \bar{\Theta} / \delta \quad (5)$$

$$R_{\text{Tot}} \equiv \sim P^{1/2} / N + \delta / \bar{\Theta} \quad (6)$$

In a multilayered membrane the total transport resistance of a membrane, R_{Tot} , is the sum of the resistance in each layer ($\delta_M / \bar{\Theta}_M$) plus the effective resistance caused by gas-phase diffusion.⁶

Permeabilities of the refractory metals vanadium, tantalum, zirconium, and niobium are so large that until recently they were inferred only from diffusivity and low concentration solubility coefficients via eq 4. These values are shown in Figure 1 along with experimental values for several nonrefractory metals. Recent measurements have confirmed the prediction that these metals are significantly more permeable than palladium.^{10,16} Figure 1 shows $\bar{\Theta}_M$ for some metals increasing with decreasing temperature. This temperature dependence occurs when hydrogen absorption is more exothermic than the activation energy for diffusion is endothermic, e.g., with palladium-coated zirconium.¹⁰

In polymer and porous ceramic membranes, flux is proportional to $\sim P$, not to $\sim P^{1/2}$ as with metal membranes. Because of this, metal membranes are more attractive at low hydrogen pressures. This is seen by approximating for $\sim P^{1/2}$ from the derivative with respect to P ,

$$P^{1/2} \approx \sim P / 2P^{1/2}$$

where P is the average hydrogen partial pressure. Combining this with eq 3 for flux through a metal membrane

$$N \approx (\bar{\Theta}_M / 2 \delta_M) P^{1/2} \sim P$$

flux per pressure drop decreases with increasing hydrogen pressure. In a polymer or ceramic this permeance is measured in barrers and is fairly pressure independent.

High hydrogen concentrations tend to decrease a metal's diffusivity but increase its Sieverts constant.^{17,20} The hydrogen diffusivity decreases because the nearest-neighbor sites for hydrogen atom jumps become filled.²⁰ Because hydrogen concentration increases with decreasing temperature, this effect tends to flatten the temperature dependence of the hydrogen permeability. The Sieverts constant rises with increasing concentration because the hydrogen atoms attract. The net effect is that fluxes are effected little but often vary from the pressure to the $1/2$ expectation. Palladium-coated tantalum and niobium disks show permeabilities similar to Figure 1, but the temperature effect is flattened.¹⁶ This paper will discuss pressure effects.

Gas-phase transport resistance, surface resistance (dissociation/recombination), and interface effects can also affect transport,^{13,21,22,27} and several modifications of eq 3 include these resistances.^{7,21,22} With proper coating, though, interface resistance can be removed almost completely.^{13,23} Similarly, dissociation on palladium presents little transport resistance even at temperatures as low as 325 °C¹⁰ unless fouling is present. Palladium is fairly immune to surface poisoning,^{28,30} but since these membranes are so permeable, they may foul with impurity concentrations that would go unnoticed with homogeneous palladium or alloys. Also, because the membranes are extremely permeable and are 100% selective, gas-phase mass transport resistance can appear at flows and geometries which would be inconceivable with other membranes.

The experimental setup is shown in Figures 2 and 3. We use tubular membranes rather than the flat disks used previously¹⁶ because tubes allow a thinner wall for

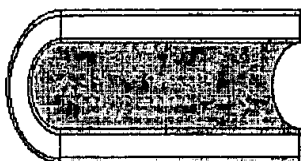


Figure 2. Cutaway diagram of a tubular membrane.

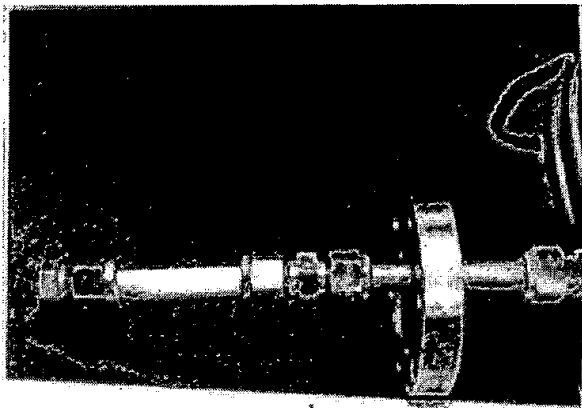


Figure 3. Photograph of a membrane in a Swagelok holder.

a given pressure differential, and thus allow higher hydrogen fluxes. Also, tubular membranes are easily fabricated into large-scale hydrogen extractors using a shell-and-tube heat-exchanger design.

Most of the experiments presented here use tantalum because tantalum showed less hydrogen embrittlement. Niobium is somewhat cheaper and more permeable to hydrogen than tantalum but is more readily embrittled.¹⁶ Several alloys have shown higher hydrogen permeability than these elements and avoid hydrogen embrittlement entirely, but none are as readily available in tube form.

Preparing, Coating, and Evaluating Tubular Membranes

We started with commercial-grade tantalum heat-exchanger tubes $\frac{3}{8}$ in. in diameter in four wall thicknesses (0.054, 0.037, 0.027, and 0.007 cm) and with a niobium tube ($\frac{3}{8}$ -in.-diameter, 0.034-cm wall). Tube lengths were between 4 and 41 in. The surfaces of these tubes arrive from the manufacturer coated with a layer of oxide and often with a layer of oil. Both of these interfere with the coating process and must be removed in order to make an acceptable membrane. Gross oxide and oil was removed by abrasion and detergent. We then electropolished, hydrided, and applied our electroless palladium coat as described previously.¹⁵ For several of the coated tubes, we used hydrazine as the reducing agent instead of hypophosphate. Hypophosphate was found to deposit palladium 5% phosphorus,^{24,25} and we hoped to find superior performance with a purer palladium coat produced by reducing with hydrazine.

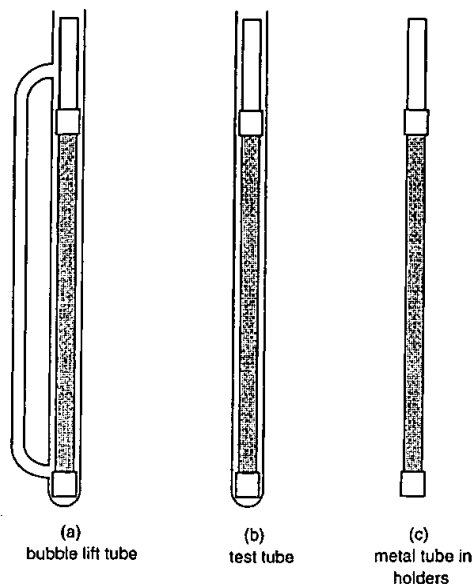


Figure 4. Electroless coating setups.

With several tubes the solution was mixed continuously during plating by performing the plating in a test tube with a side arm (Figure 4a). Here, gas that evolves during coating causes an upward flow of solution, and the side arm allows a return flow once the bubbles leave (gas-lift circulation). We thought such circulation might improve the coat. The rest of the membranes were coated in large test tubes (Figure 4b) and stirred only occasionally. In all, we coated more than 60 tantalum tubes and 20 niobium tubes.

Several membranes were annealed at high pressure (HIPing) by sealing the apparatus exits and pressurizing with 100 psi of argon. Membranes were heated to 500–525 °C and kept this way for several hours or days to see whether higher hydrogen fluxes resulted from an improved bond between the palladium and the substrate. Sawatzki and Ledoux¹⁴ found that annealing for 4 h at 700 °C improved hydrogen removal from a palladium-coated zirconium tube, presumably because of increased bonding.

Permeability and Durability Measurement

The permeabilities of the palladium-coated metal membranes were studied using the apparatus shown in Figures 5 and 6. The membranes were reliably sealed into the apparatus via swageloks (Figure 5). We use graphite ferrules to allow the membrane to swell without stress embrittlement or leaks.

Impure hydrogen gas, or a mixture of hydrogen and argon, enters the apparatus as indicated by the arrows in Figures 5 and 6. The gases travel up the outside of the module while being heated to operation temperature, they then flow down the inside of the apparatus and contact the membrane. Much of the hydrogen permeates the membrane, and the rest exits along with the argon or impurities. We measure the flow rate of hydrogen through the membrane and the gas pressures at the inlet and exits (Figure 6). From this and the membrane area, we calculate the effective permeance of the membrane via eq 5. The total membrane resistance is then the inverse of the permeance and equals the sum of mass-transfer resistances in the palladium, in the tantalum, in the interface (if any), and in the

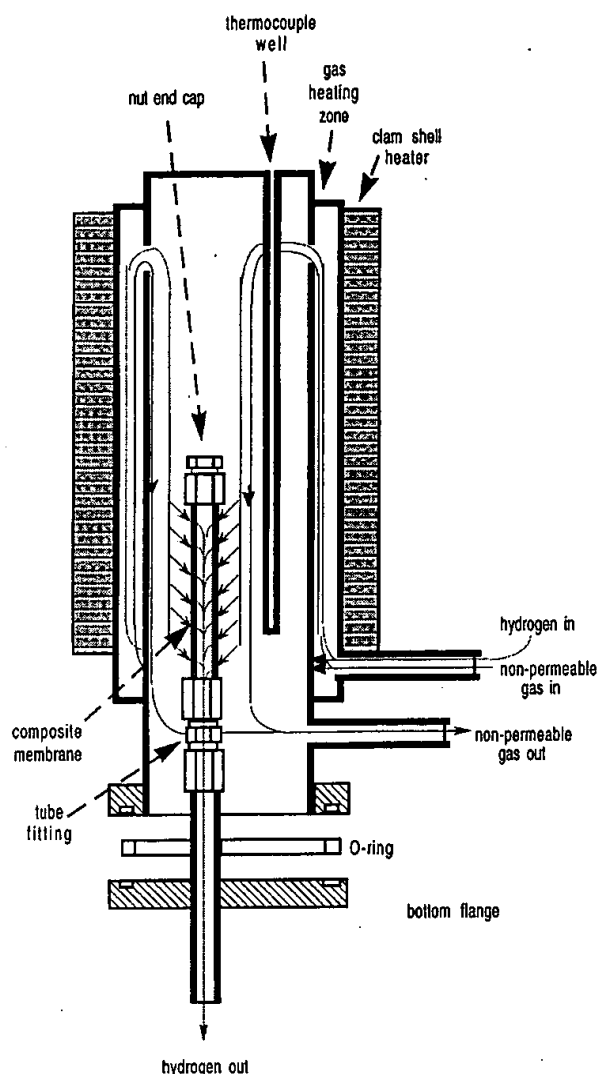


Figure 5. Membrane permeation apparatus.

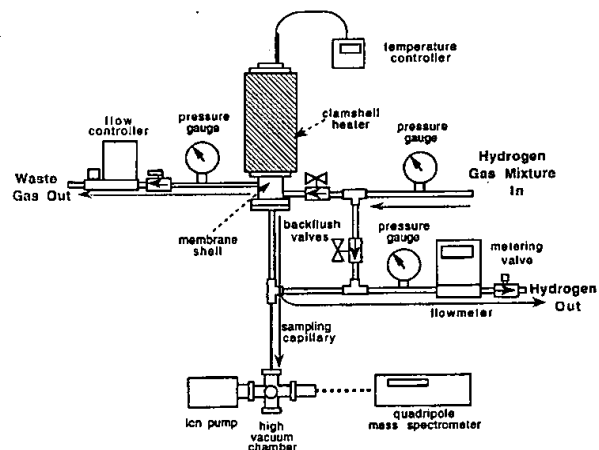


Figure 6. Membrane test apparatus showing flows.

flowing gas stream. The effective membrane permeability is calculated from the permeance and thickness via eq 5.

Durability tests involved measuring the permeation flux continuously for several weeks. During durability testing membranes were given weekly backflushes with hydrogen to drive off coke and other contamination that

may have agglomerated on the upstream membrane surface. Backflushing was done by reversing the hydrogen flux through the membrane.

As with our earlier experiments,¹⁰ we regularly check for leaks by analyzing the output hydrogen purity, here using an on-line mass spectrometer (Figure 6). Any sign of argon in the output is evidence of a leak, and we shut down. Except when testing for leaks, the membrane is run with Matheson 99.8% pure hydrogen as a feed and 98% hydrogen (approximately) as a purge. This purity was chosen to minimize gas-phase mass-transfer resistance, while getting an industrially-significant measure of the permeance. Gas-phase mass-transfer resistance can be very large with these membranes because of the very high hydrogen fluxes.

Electron Microscopy, X-ray, and Auger Spectroscopy

Electron microscopic and X-ray examination of the coat was used extensively because it gave an excellent image of coat thickness and uniformity at the magnifications of interest, about 5000 \times . A combination of Auger and X-ray spectroscopy was used to determine elemental compositions of the coat and of the interface. Auger spectroscopy was used to determine that there were no foreign elements at the surfaces or interfaces, but because of the small spot size, it is easily confused by oxygen or water that adheres to the sample surface during mounting. X-ray spectroscopy scans a much larger volume, making it more accurate for studying coat composition, but it is insensitive to all but the grossest interdiffusion effects, and it is blind to oxygen, nitrogen, and carbon contaminants.

Results: Solution Coating and Stirring

We coated several 18 in. long membranes in the simple test tubes (Figure 4b), stirring occasionally by hand. We coated several others (including the largest membrane, 41 in. long) using gas-lift solution circulation (Figure 4a). In either apparatus a 16 3 3m palladium coat requires from 4 to 12 h. We could detect no improvement in coat quality from gas-lift circulation, and since this technique is cumbersome, we recommend using simple test tubes.

The coat formed more readily using hydrazine as the reducing agent instead of hypophosphate. The composition of membranes using Auger spectrometry showed that the Pd coats produced using hypophosphate contained 5% phosphorus impurity and showed some metallic interdiffusion at 420 $^{\circ}\text{C}$. The newer hydrazine-based coats showed no detectable impurities and no clear sign of interdiffusion. Figure 7 suggests that the transport resistance is somewhat lower with hydrazine as well.

After long periods of operation, especially at high temperatures, the palladium surface tended to turn darker than at first. Auger, electron microscope and X-ray analysis comparing membranes before and after operation showed no clear sign of interdiffusion but showed a surface morphological change. Apparently, we are making "palladium black", the palladium equivalent of platinum-black catalyst. This increased surface roughness may explain the observation that flux increases during the first few hours of operation and eventually decreases (see below). Figure 3 shows a membrane after 31 days of operation at 420 $^{\circ}\text{C}$; surface darkening is seen at the tube end near the ferrule. We

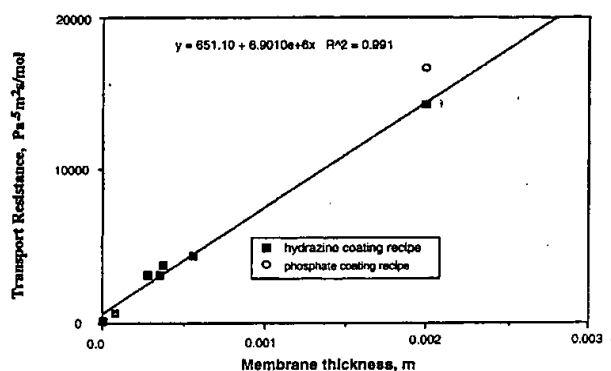


Figure 7. Transport resistance in palladium-coated Ta membranes at 420 °C; two coating recipes.

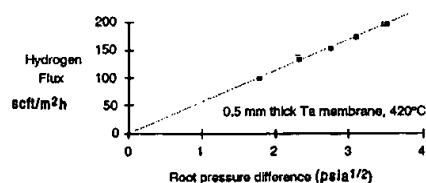


Figure 8. Hydrogen flux vs. root pressure difference.

suspect that surface darkening is caused by defect migration from below. These defects may have been caused by expansion of the palladium or refractory metal during hydrogen absorption.²⁷ We could test this hypothesis by replacing the pure metal palladium and substrates with less defect-prone alloys or by charging the substrate with different amounts of hydrogen before coating.

When observed with Auger spectroscopy, all coats showed significant surface carbon and oxygen. This contamination is probably due to exposure to the atmosphere during sample mounting and is probably not representative of the permeation environment.

Membrane Permeability

Figure 7 plots the effective resistance of several membranes as a function of refractory metal thickness. As expected from eq 6, resistance increases in proportion to membrane thickness, but Figure 7 also suggests that transport resistance is somewhat higher with the older phosphate recipe than with the newer recipe. A positive intercept is expected in this plot, representing transport resistance through the palladium coat, surfaces, and interfaces. The correlation coefficient for the linear fit is 0.991, including only membranes coated by the newer recipe.

The slope of the line in Figure 7 should be inversely proportional to the tantalum permeability for any fixed surface or palladium transport resistance (eq 3), i.e., $\bar{D}_M + 1/(\sim R_M + \sim c_M)$. Surface and fixed palladium-layer resistances affect only the intercept of this line, assuming only that they remain constant throughout. Thus at 420 °C, the average permeability of tantalum equals $1/6.901 \times 10^6$ or 1.45×10^{17} mol/m s Pa^{1/2}. This value is in close agreement with Figure 1. Our previously reported value for the permeability of tantalum was 30% lower,¹⁶ but this value was not corrected for surface resistance.

Figure 8 shows the hydrogen flux with a thick-walled palladium-tantalum membrane as a function of pressure differential at 420 °C. The upstream pressures ranged from 1 to 3 atm, and downstream pressures ranged from

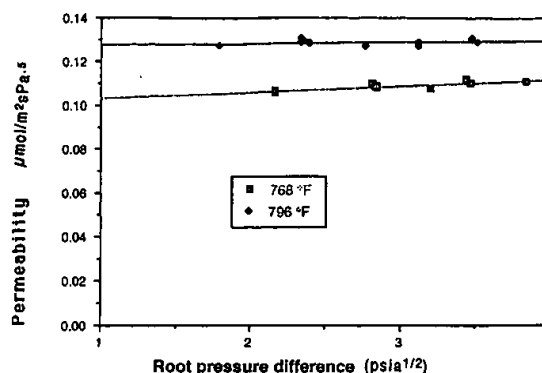


Figure 9. Tantalum membrane permeability vs temperature and pressure.

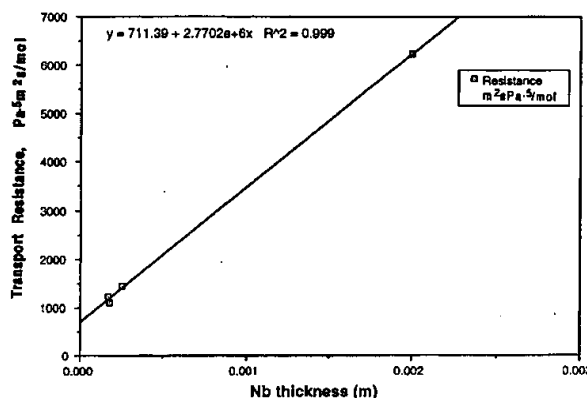


Figure 10. Transport resistance in Nb-based membranes vs membrane thickness.

near vacuum to about 1.5 atm. For all driving pressures studied, flux is nearly proportional to pressure difference to the $1/2$ power, agreeing with eq 3. The average effective permeability here is 1.2×10^{17} , somewhat lower than the above because of resistance in the palladium coat and at the palladium surfaces. Still this is 10 times higher than the permeability of palladium alloys at this temperature, about 1.2×10^{18} mol/m s Pa^{1/2}. Even with thin-walled palladium membranes, the flux is about $1/5$ the values in Figure 8.

Figure 9 shows the effective permeability of a palladium-coated tantalum membrane as a function of pressure at two temperatures. At both temperatures, it appears that permeability is fairly independent of hydrogen pressure. This is not to say that \bar{D}_M and K_S are pressure-independent, only that the product of \bar{D}_M and K_S varies only weakly with H concentration at these temperatures. The permeability is seen to increase with temperature, contrary to the prediction in Figure 1 but in agreement with our previous findings.¹⁹

Niobium Membranes

Niobium heat-exchanger tubes up to 18 in. long were coated with palladium using the same techniques used for the tantalum tubes above. The transport resistance with these membranes is shown in Figure 10. As with tantalum, transport resistance in Nb-based membranes increases linearly with thickness in accordance with eq 5. The intercept resistance in Figure 10 is higher than with tantalum (Figure 7). This higher intercept with niobium may reflect surface resistances or may represent a poorer coating technique. The average permeability in niobium, determined from the slope of the line

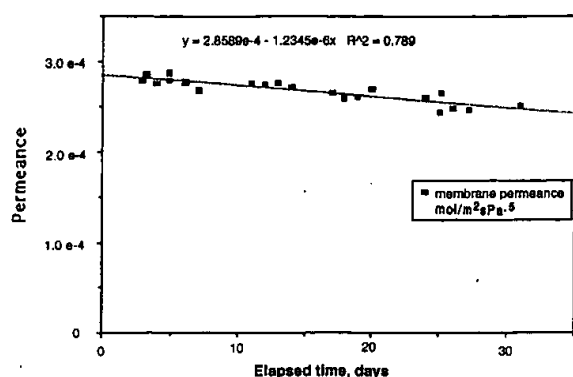


Figure 11. Permeance of a palladium-coated tantalum membrane run for 31 days at 420 °C with weekly backflushes.

as above, is 3.6×10^{47} mol/m s Pa^{1/2}. This is 2-1/2 times the permeability of tantalum and is almost identical to the value measured using thick niobium disks.¹⁶ This value, however, is about half the prediction in Figure 1.

The maximum permeance of our Nb-based membranes was 0.0011 mol/m² s Pa^{1/2}, 75% that of the thinnest-wall tantalum-based membranes. This lower permeance could be improved if thinner walled niobium were used; the thinnest-wall niobium membranes were 0.15 mm thick, twice the thinnest-wall tantalum membranes.

Membrane Durability

Commercial membranes should last a few months to a few years in service with only minimal loss of flux. To test our membrane's durability, we measured the flux in several membranes for periods up to 31 days.

A tantalum-based membrane that was run for 31 days at 420 °C is shown in Figure 3. It looks like new except for a slight darkening near the upper ferrule as discussed above. Figure 11 shows that the permeance of this membrane decreases with time, decreasing about 15% over 31 days of operation. The decrease is approximately linear with time, varying only slightly on a daily basis, presumably due to variations in gauge readings, atmospheric pressure, and the effect of weekly backflushes. Weekly backflushing with hydrogen is found to increase the flux by a few percent. Membranes coated using the older phosphate recipe deteriorated somewhat faster, possibly because of the difficulty in getting a good coat.

Hydrogen embrittlement was a serious problem with tantalum and niobium membranes. The minimum temperature for tantalum membranes was 350 °C, dictated by the need to avoid embrittlement cracking. The minimum temperature for niobium membranes was 420 °C for the same reason. Cracking is also affected by hydrogen pressure, metal annealing, and thickness and by the tightness of the ferrules.

Discussion

The flux with these membranes is about that predicted from theory and earlier experiments but increases with temperature, contrary to our simple expectations for Ta and Nb. Two effects may cause this behavior. First, the palladium coat adds a resistance and this resistance decreases with increasing temperature. Further, as temperatures increase, the hydrogen content decreases and this increases diffusion rates by

increasing the number of vacant sites next to the hydrogen atoms.²⁰ These two effects could cause the rise in effective membrane permeability for the pressures and Pd thicknesses studied.

The thinnest membranes, made from 0.07 mm wall tantalum tubes, show transport resistance of 700 m² s Pa^{1/2}/mol (permeances of 0.00147 mol/m² s Pa^{1/2}). Fluxes with such membranes are higher than those with any other nonporous membrane that we know of and continue to increase with decreasing tantalum thickness. This suggests that the major transport resistance is in the substrate, at least for the membrane thicknesses studied.

The flux is higher than with the commercial polymeric membranes, but the cost seems higher as well, currently this is about \$500/ft² as compared with \$200/ft² for polymers.³¹ Thus, flux and price are in the range for economical application. Scaleup and fabrication do not seem to be a serious problem since the coating methods are simple. The membranes are attached by standard swageloks. The 15% decrease in flux for 31 days is a serious concern, though, since the root causes are not clear at this stage.

Membrane life will have to be extended to 1 year or so before they are ready for commercial use. If transport resistance adds at the steady rate of 15%/month, as appears from Figure 11, the membrane flux would fall below 50% in 667 months. We have tried several "cures" at this stage, and none has worked completely. Presuming that the cause was small amounts of impurity concentrating at the metal surface (fouling), we tried backflushes as described above. This helped but did not completely erase the deterioration, possibly a longer backflush is needed. Alternatively, if the observed morphological changes caused deterioration, maybe a low-swelling alloy would deteriorate slower than the pure metals used here. Alternatively, deterioration may be due to interdiffusion of the palladium and substrate as suggested by Edlund.²⁶ This is the "best result" since interdiffusion would tend to slow on its own as the interdiffusion layer grew. Thus, the membrane tested in Figure 11 might be expected to operate for years before the flux dropped 50%. Edlund et al.²⁶ found evidence for intermetallic interdiffusion at 700 °C, but the flux decrease in Figure 11 looks too steady for this explanation. Deterioration shows no slowing as the interdiffusion zone increases, but our experiments were of short duration. Longer term experiments will show whether interdiffusion is the cause.

In a preliminary experiment we were able to reverse this deterioration completely by replacing the palladium surface with fresh palladium. More experiments are being conducted in this area.

Sample Design, Hydrogen Extraction from Hydrotreater Off-Gas

Hydrogen is used in petrochemical plants for hydrodesulfurization and for methanol and ammonia synthesis. Additional hydrogen has a value in such plants because it reduces plant energy costs and allows more flexible operation, e.g., it allows production of a "reformulated" gasoline that maintains current octane levels but has fewer aromatics (aromatics are carcinogenic, polluting components of gasoline). A common route to reformulated gasoline is to reduce the flow and temperatures in reformer units while increasing the flow and temperature in Catcracker fluidized-bed reactors.

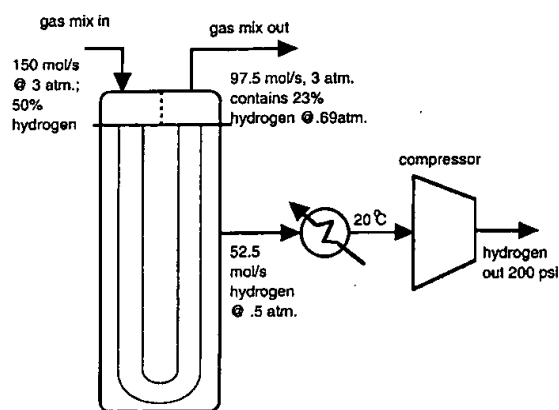


Figure 12. Setup for hydrogen removal from hydrotreater off-gas.

This change reduces the amount of reformer hydrogen available for hydrodesulfurization and resid upgrading, so this route requires a source of additional hydrogen. Depending on the plant, pure hydrogen has a chemical value about \$2.00/kg mol (\$0.002/g mol) above its fuel value.^{26,27}

We will consider a modestly large stream of hydrotreater off-gas: 10 000 000 scf/day at 3 atm, containing 50% hydrogen mixed with methane, ethane, water, and CO₂. Refineries produce and burn such streams as "fuel gas" because the low-pressure hydrogen is too expensive to recover. We will recover 70% of this hydrogen using a metal membrane-based extractor in the shape of a shell and tube heat exchanger (Figure 12). The gas mixture flows through the tubes, while the hydrogen is recovered from the shell. The double-pass, vertical-standing design minimizes problems of metal expansion and membrane support. In SI units, the flow is 150 mol/s, with hydrogen making up 75 mol/s; if 70% is recovered, this is 52.5 mol/s (3.5 MMscf/day).

For a benchmark design, consider 420 °C operation, using 1 cm diameter tubes of our best current palladium-covered tantalum. These tubes have a permeance of 0.001 47 mol/m² s Pa^{1/2}, are strong enough for the pressures and temperatures needed, and, because of their large diameter, add minimal gas-phase pressure drop. Still, the hydrogen pressure in the shell must be lower than the minimum hydrogen partial pressure in the tubes since this pressure difference drives the extraction. The minimum hydrogen pressure in the tubes is:

$$\text{H}_2 \text{ partial pressure} + \frac{(3 \text{ atm}) \times (22.5 \text{ mol/s unrecovered H}_2)}{97.5 \text{ exiting mol/s}} + 0.69 \text{ atm} \quad (7)$$

For design purposes, pick a hydrogen shell pressure of half this, 0.35 atm. (It is generally recognized that polymer membranes are not economical at such low-pressure gradients.)

The membrane surface area is calculated from the permeance, 0.001 47 mol/m² s Pa^{1/2}:

$$\text{flux, } N = \frac{52.5 \text{ mol/s}}{\text{area}} + P_{\text{up}}^{1/2} \text{ } \phi \text{ } P_{\text{dn}}^{1/2} \text{ (permeance)} \quad (8)$$

where P_{up} is the average hydrogen partial pressure in

the tube, P_{dn} is the hydrogen pressure in the shell, and 52.5 mol/s is the design load. P_{up} varies between 1.5 atm at the tube inlet and 0.69 atm at the tube outlet, but for eq 8, let us use the geometric average 1.0 atm, or 100 000 Pa in SI units. The downstream hydrogen pressure is 0.35 atm, or 35 000 Pa. The flux is thus

$$N = (316.2 \phi 187.1 \text{ Pa}^{1/2})(0.00147) + 0.190 \text{ mol/m}^2 \text{ s}$$

From eq 7, the membrane area is

$$A = (52.5 \text{ mol/s}) / (0.190 \text{ mol/m}^2 \text{ s}) + 276 \text{ m}^2$$

For an extractor of this area, the shell could be 5.5 m long, containing doubled tubes 10 m long. Since each 1 cm diameter \times 10 m tube has a surface area of 0.314 m², the extractor will use 880 tubes for a total tube length of 8800 m, or 27 500 ft. The shell diameter for this number of tubes would be about 1 m.

A series of intercooled compressors is now chosen to bring the hydrogen to 200 psi for general plant use. Steam sparging is a cheaper alternative for the first stage of hydrogen compression, but it contaminates the hydrogen with water vapor.

Economics of Hydrogen Recovery with This Extractor

The adiabatic pumping cost is estimated as the isothermal compression work at 400 K, an average gas temperature assuming inefficient intercooling.

$$W = RT \ln(P_f/P_i) + 8.314 \times 400 \times 3.660 + 12 \text{ kJ/mol} \quad (9)$$

At 7.5¢/kwh this operating cost is 0.025¢/mol.

The total equipment cost is now calculated from the cost of tubes, shell, pumps, etc. Large runs of uncoated tantalum tubes are priced at about \$15/ft. Coating 1 3m of Pd on each side is estimated to add an additional \$5/ft, and thus the membranes cost about \$20/ft, or 0.55 M\$ total. Added to this are the purchase cost of the shell, fabrication, control, and heat exchanger, an additional \$200 000. The projected capital cost excluding pumps is thus 0.75 M\$, which is increased to 1.25 M\$ including the price of rotary vane pumps.

This capital cost must be compared to the value of the recovered hydrogen minus operating costs. Assuming the hydrogen is worth 0.2¢/mol more than its fuel value and operating costs are 0.025¢/mol as calculated above, operating profit is

$$(52.5 \text{ [mol/s]}) \times (0.002 \phi 0.000 25 \text{ [$/mol]}) \times (3.15 \times 10^7 \text{ [s/yr]}) + 2.9 \text{ M$/yr}$$

Given the capital cost of 1.25 M\$, the payback period is less than 5 months, which is excellent. The calculations can be redone using our current membrane cost, \$45/ft, and the payback period is found to be less than 8 months, which is still excellent. Optimization should result in improved economics.

Acknowledgment

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Hydrogen transport through non-porous membranes of palladium-coated niobium, tantalum and vanadium

Robert E. Buxbaum^{a,*} and Terry L. Marker^b

^aDepartments of Chemical Engineering and Physiology, Giltner Hall, Michigan State University, East Lansing, MI 48824 (USA)

^bUOP, 25 E. Algonquin Rd., Des Plaines, IL 60017 (USA)

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Abstract

Experiments are reported for hydrogen transport in palladium-coated membranes of niobium, tantalum, and vanadium. Two geometries are studied, coated discs 2 mm thick, and coated tubes of 0.25 mm wall thickness. The hydrogen is extracted at 100% purity. Fluxes are much higher than with current palladium alloy and polymeric membranes at these pressures, and are somewhat higher than with palladium-coated porous ceramics. Palladium-coated niobium discs show effective permeabilities about 0.32 $\mu\text{mol}/\text{m}\cdot\text{sec}\cdot\text{Pa}^{1/2}$ at 425°C and 2 atm pressure (including gas-phase resistance). The coated tubes have about 1/2 this permeability, and thus mass transport resistances about 1450 $\text{m}^2\cdot\text{sec}\cdot\text{Pa}^{1/2}/\text{mol}$. Coated tantalum discs have effective permeabilities about 0.1 $\mu\text{mol}/\text{m}\cdot\text{sec}\cdot\text{Pa}^{1/2}$, but are less susceptible to hydrogen embrittlement. Since these coated-metals are stronger and more durable than palladium, ceramics or polymers, considerable design flexibility is possible. Based on these measurements, the flux for advanced membranes would be 2000 $\text{scf}/\text{hr}\cdot\text{m}^2$ for a driving force of 3 atm, suggesting attractive economics for petrochemical plant use.

Key words: composite membranes; gas separations; metal membranes; hydrogen

Hydrogen transport in metals

From a theoretical prospective, several common metals should be more permeable to hydrogen than is palladium, a metal widely used for hydrogen purification and extraction [1,2]. These metals are not used for hydrogen extraction because, until recently, the experimental fluxes fell far short of the predicted values.

Hydrogen transport in a metal membrane can

be predicted from the diffusion coefficient and the concentration gradient:

$$N_H = -D_M(\Delta C_H/d_M), \quad (1)$$

where N_H is the flux of hydrogen atoms, D_M is diffusivity of hydrogen in that metal, ΔC_H is the change in hydrogen atom concentration across the membrane, and d_M is the membrane thickness. If the dissolved hydrogen atoms are in rapid equilibrium with hydrogen molecules the gas, C_H is related to the hydrogen pressure on either side of the membrane via Sieverts thermodynamic relation:

$$C_H = K_S(P^{1/2}). \quad (2)$$

*To whom correspondence should be addressed. Tel.: (+1)(517) 353-5383; Fax: (+1)(517) 355-5125.

Here, K_S is the Sieverts constant and P is the partial pressure of hydrogen in equilibrium with the metal. The power of $1/2$ derives from the dissociation of each hydrogen molecule into two independent hydrogen atoms. Combining eqns. (1) and (2), and recalling that the flux of hydrogen molecules is half the flux of atoms:

$$N = -[D_M K_S / 2] (P_{up}^{1/2} - P_{dn}^{1/2}) / d_M. \quad (3)$$

This is known as Richardsons equation, and the term in square brackets is called "the hydrogen permeability". This term is plotted in Fig. 1 as a function of temperature for several metals [2]. As Fig. 1 shows, the hydrogen permeability of several refractory metals, niobium, tantalum, zirconium and vanadium, is more than an order of magnitude higher than available with palladium, a metal widely used for hydrogen extraction. For uncoated refractory metals, it appears that surface resistances slows hydrogen entry and exit from the metal [3-6]. This shifts the surface-gas equilibrium, eqn. (2), undermines the $\Delta P^{1/2}$ behavior of eqn. (3) [15], and reduces transport.

Several attempts have been made to reduce

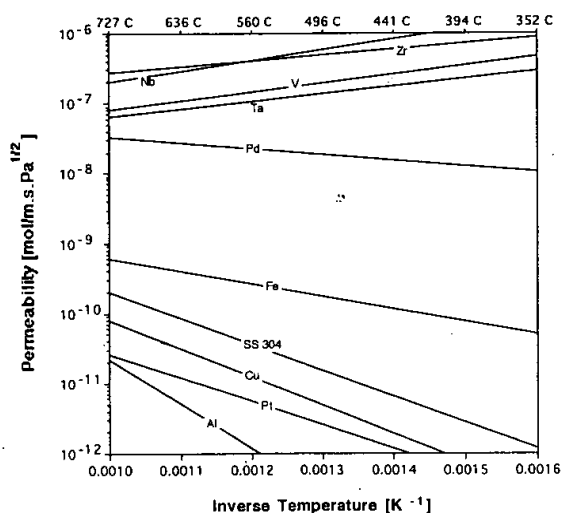


Fig. 1. Hydrogen permeabilities of selected metals. Data from Steward [2].

the surface resistance of these metals by annealing in high vacuum, and by ion bombardment. These treated metals do not show the transport rates of Fig. 1 [3-7] suggesting that the surface resistance is fundamental to these metals [4-7], or is caused by a very tightly held oxide which impedes absorption [3,7]. If this surface resistance could be removed, these refractory metals could provide hydrogen extraction membranes with exceptional transport properties, and at a considerably lower price than palladium or its alloys [8]. Since these metals are stronger than palladium, the membranes could be made thinner-walled as well. Flux should be inversely proportional to membrane thickness, eqn. (3), and thin-walled membranes could have fluxes that are two orders of magnitude greater than available with palladium. The hydrogen purity is expected to be 100% since, at these temperatures, metals are impermeable to all gasses except hydrogen.

In 1967, Makrides et al. demonstrated that surface resistances of refractory metals could be reduced significantly by first cleaning, and then vapor-depositing palladium on the entrance and exit faces [8]. Palladium is thought to catalyze the molecular hydrogen dissociation and recombination reactions, and to decrease the transport barrier for hydrogen atom absorption into the refractory metal [4-6,8,9]. Further, the palladium layer protects the refractory metal from oxidation while handling in air [8,10].

We have attempted to improve on the vapor-coated membranes of Makrides et al. Those membranes, it turned out, were hard to coat, and had properties that varied widely (compare the results in refs. [3,4,8]). In our laboratory, the refractory metals are coated with electroless palladium on their entrance and exit faces, and annealed in hydrogen at 400°C for at least 1 day. This annealing step may serve to remove oxides from the palladium surface [9],

and from the palladium-refractory interface. Also, annealing may weld the palladium to the refractory substrate, providing a shorter, wider diffusion path [10]. Our experiments use palladium thicknesses of 1-2 μm since theoretical analysis [11,12] suggested that such thicknesses would provide durable membranes, while adding modest mass-transport resistances [12]. We use the palladium coating recipe of Hsu and Buxbaum [13], with the addition of an electrochemical surface hydriding step that was found to be necessary to make the coating adhere [14]. An advantage of electroless coating is that it is well suited to application on commercial, tubular membranes; large, tubular membranes are easier to coat by electroless deposition than by any other technique. This recipe is found to apply an appropriate layer of palladium within 2 hr [13]. The palladium-coated metal membranes are then stable to handling in air, and are easily fabricated into structures for experimental measurement. We have attached such membranes to stainless steel by Swagelok and ConFlat® flanges, for tubular and flat membrane geometries respectively.

Previous experiments in our laboratory [15] studied hydrogen transport through 2 mm thick palladium-coated zirconium discs. We determined that the permeability of the zirconium layer was $P_{\text{Zr}} = 2.00 \times 10^{-6} \exp(59/T) \pm 40\%$ mol/m-sec- $\text{Pa}^{1/2}$ at temperatures from 600-700 K (323-423°C), and that the sticking coefficient for hydrogen interaction with the palladium surface was about 0.04 at these temperatures. Hydrogen transport in these zirconium discs was 2 orders of magnitude greater than in the same thickness of palladium at these temperatures. The membranes were stable for a month despite the fact that one side was exposed to an oxidizing atmosphere.

Experimental procedure

The apparatuses for experimental measurement of hydrogen permeation in flat mem-

branes of niobium and tantalum is shown in Fig. 2, and for tubes of coated niobium in Fig. 3. Our older equipment was used to measure hydrogen permeation in palladium-coated vanadium; this equipment has been described previously [15].

To measure the permeability of hydrogen through palladium-coated discs, we started with rods of niobium, tantalum and vanadium (A.D. Makay); these were machined into discs 2.4 cm^2 area and generally 2 mm in thickness (about the size of a US nickel). These discs were then cleaned with steel wool, ultrasonic soap bathing, and solvents, and then coated with electroless palladium as described previously [14]. Typical palladium coats thickness were 1-2 μm , measured gravimetrically. These coat thicknesses were chosen to maintain a high membrane durability without greatly impeding hydrogen transport [12]. Disc membranes are mounted within the flow chamber, Fig. 2, with the knife edge connectors shown. The membranes are then heated to temperature under vacuum. Once the membranes are at temperature, they are exposed to flowing gas mixtures and annealed. This start-up is used to avoid

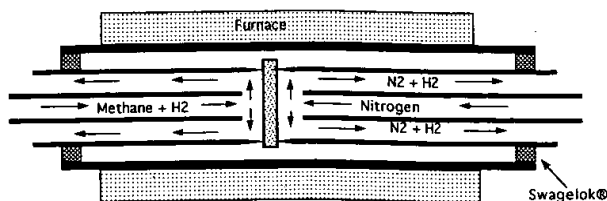


Fig. 2. Apparatus used to measure hydrogen transport through palladium-coated discs of niobium and tantalum.

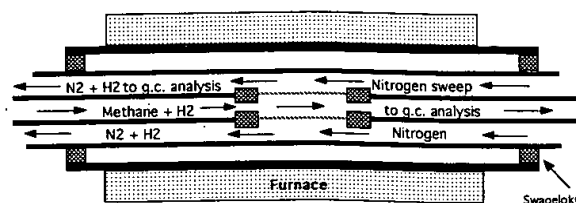


Fig. 3. Apparatus used to measure hydrogen transport through palladium-coated tubes of niobium.

swelling and hydrogen embrittlement that might otherwise destroy the membrane seals or the membranes themselves [1,16]. The discs are annealed in place before proceeding to remove detrimental oxides at the palladium surface [9], and to improve the bond at the palladium-refractory interface [10].

The procedure with the tubular membranes was similar. We started with tubes of niobium. These were cleaned inside and out with steel wool and with a steel brush mounted on an electric drill. This was followed by the surface treatment and coating procedure, as above. The membranes were then sealed into the test apparatus, Fig. 3, by means of swagelok connectors. Graphite ferrules were used to avoid cracking the membrane during start-up and shut-down; graphite has more give than standard stainless, or brass ferrules.

Experiments were carried out for several days with each membrane, or until the membrane cracked. The upstream surface of the membrane is exposed to a flowing mixture of 75% hydrogen and 25% methane at about 3 atm. The downstream surface is exposed to a sweep gas of flowing nitrogen. Mass flow rates were about 150 cm³/min on the upstream surface, and about 100 cm³/min on the downstream surface. We calculated the membrane flux from measurements of the mass flow rates and from the concentration of hydrogen in gas samples that were removed regularly from before and after the membrane. These samples were removed, both from the source gas mixture, and from the sweep nitrogen, and were analyzed for hydrogen content by gas chromatography. We also used the gas chromatographic data as a continuous check for leaks: if methane is found in the sweep nitrogen, or if nitrogen is found in the source gas, this would indicate a leak and the experiment was stopped.

The effective transport resistance was calculated from the flux (determined above), and the average hydrogen pressure on the upstream

and downstream face of the membrane. The effective hydrogen permeability of the membrane was then calculated from this resistance and the total membrane thickness. Effective resistances and permeabilities calculated in this way represent averages from permeability in the palladium and the substrate; these averages are further reduced by gas-phase mass-transfer resistance [12,15], discussed below.

Experimental results

Figures 4 and 5 show the flux of hydrogen through discs of palladium-coated niobium and tantalum respectively; on the left side of these figures we show the experimental hydrogen fluxes, on the right side, we show the average hydrogen permeability of the disc. This is lower than the permeability of the niobium substrate since there is transport resistance in the palladium, in the interfaces, and in the gas-phase. From Fig. 4, the effective permeability of the

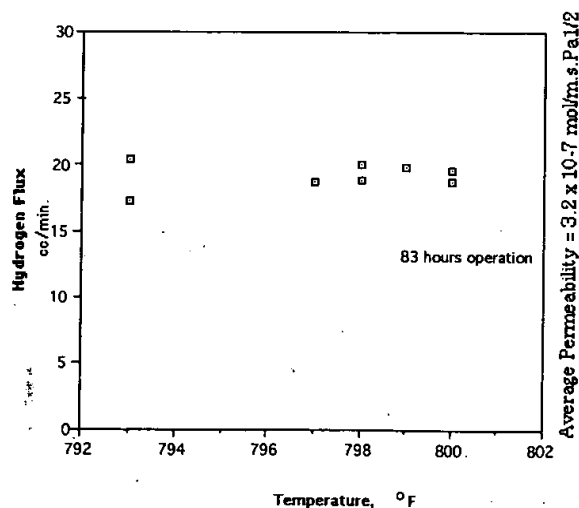


Fig. 4. Hydrogen flux and effective permeability with a palladium-coated niobium disc as a function of temperature; disc is 2.4 cm² area, 2 mm thick, 2 μ m palladium coat on both faces, $\Delta P_{H_2} = 40$ psia (73% hydrogen in methane) - 2 psia (10% hydrogen in nitrogen).

palladium-coated niobium disc is 3.2×10^{-7} mol/m-sec-Pa^{1/2}, and seems relatively temperature insensitive over the small temperature range studied. This effective permeability is considerably higher than with palladium membranes [1], or with earlier vapor-coated, unannealed refractory metals [3,8]. Still transport rates are only 1/3 of the value for niobium in Fig. 1. An attempt was made to vary the pressure difference between the membrane faces in order to see whether the square-root of pressure dependence held. Within experimental error it did, but there was too much scatter, and not enough data, to say conclusively.

As shown in Fig. 5, the permeability of hydrogen through a palladium-coated tantalum disc increases with temperature. The effective permeability is 1.0×10^{-7} mol/m-sec-Pa^{1/2}, again uncorrected for transport resistance in the palladium or gas-phase. This effective permeability is somewhat lower than with palladium-coated niobium, and is about 1/2 of the value for tantalum in Fig. 1. Palladium-coated tantalum membranes are somewhat easier to work with than palladium-coated niobium,

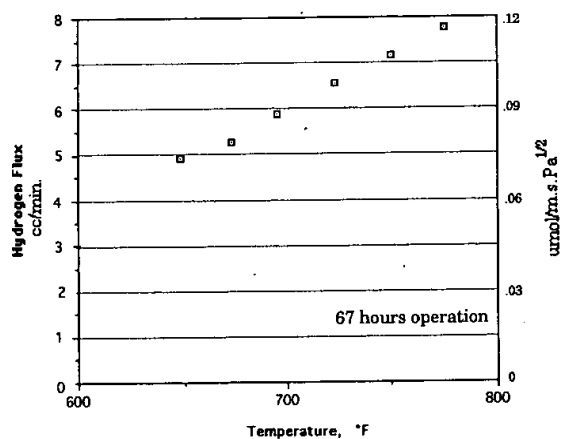


Fig. 5. Hydrogen flux and effective permeability with a palladium-coated tantalum disc as a function of temperature; disc is 2.4 cm² area, 2 mm thick, 2 μ m palladium coat on both faces, average ΔP_{H_2} = 40 psia (75% hydrogen in methane) - 1 psia (5% hydrogen in nitrogen).

being less prone to swelling or hydrogen embrittlement.

A brief set of permeation measurements was also made with a 3/8 inch diameter niobium tube (0.25 mm wall) that had been coated on the inside and outside with 2 μ m of palladium. Hydrogen flux was quite high, Fig. 6, and exceeding that for several popular polymeric membranes. The resistance to transport with this membrane was 1450 m²-sec-Pa^{1/2}/mol, indicating an average permeation coefficient of 0.17 μ mol/m-sec-Pa^{1/2}. This value is slightly lower than with the palladium-coated niobium discs, presumably because this membrane contained a higher ratio of palladium to niobium, and a higher significance of gas-phase transport resistance. (The thinner the substrate, the more significant is transport resistance in the coat and in the gas phase.) As with the discs

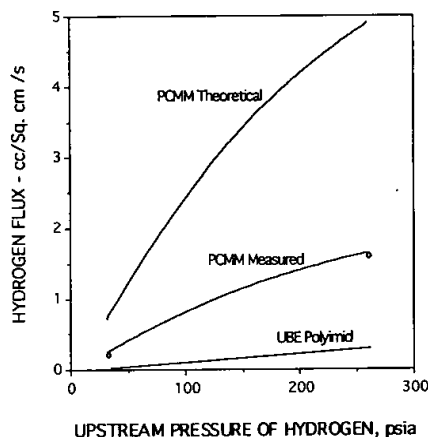


Fig. 6. Hydrogen flux with a tubular palladium-coated membrane (PCMM) 3/8" diameter, 250 μ m wall as a function of upstream pressure. Upstream gas is, on average, 16 psia hydrogen (gas mixture is 25 psia, enters at 75% hydrogen, leaves at 53%), downstream gas is, on average, 5.5 psia hydrogen in nitrogen (23 psia mixture, enters at 0% hydrogen, leaves at 48%). Also shown is the hydrogen flux with a UBE polyimide membrane at 150 °C; selectivity ratio with this membrane is 85 [20]. Theoretical value is the projected flux in the absence of gas-phase transport resistance for a 250 μ m thick Nb-based membrane, or a 120 μ m thick Ta-based membrane, with 1 μ m Pd coats on both membrane faces.

above, the effective permeation coefficient did not seem to change much with pressure.

Brief runs were also performed with two discs of palladium-coated vanadium at 400–450°C. We found average effective permeabilities of 3×10^{-8} mol/m-sec-Pa^{1/2}. This is about 1/4 the value for vanadium, Fig. 1, and is 1/10 the value with palladium-coated niobium. This coated disc showed the least difficulty with swelling from hydrogen absorption, but since the flux was lower than with the other substrates, vanadium discs were not studied extensively. At this point, we have no explanation for why there is so little permeation in coated vanadium.

In all these experiments, the membranes do not seem to degrade from the nitrogen or methane in the experimental environment.

Following completion of the permeation measurements, the membranes were analyzed via ESA and AUGER spectroscopy. These revealed that the coat contained about 5% phosphorus, and that the palladium was not face-centered cubic, as palladium generally is, but was an amorphous structure. The contamination of the palladium had been observed before [17]. We presume that the phosphorus contamination caused the palladium to plate as an amorphous layer.

Discussion of experimental results

We find that several refractory metals are very permeable to hydrogen when coated with palladium. Permeability in palladium-coated niobium does not vary strongly with temperature or pressure; permeability in palladium-coated tantalum rises somewhat with temperature between 350 and 450°C. The effective permeabilities are 1/2 to 1/3 the value of the refractory metal substrate at these temperatures, presumably because of additional resistances [12,15], as discussed below.

The hydrogen flux in these experiments can be considered to reflect a pressure driving force

and several mass transport resistances acting in series: the palladium, the substrate, the interface region, and the gas phases [15]. Thus, it is worthwhile to compare the likely individual resistances to the behavior of an entire membrane, e.g. consider the tubular niobium membrane. The effective permeance of this membrane was about 6.9×10^{-4} mol/m²-sec-Pa^{1/2} at the pressures studied; this indicates a resistance to mass transport of 1450 m²-sec-Pa^{1/2}/mol. The substrate is 0.25 mm niobium; assuming a permeability of 1×10^{-6} mol/m-sec-Pa^{1/2} [2], the mass transfer resistance of this layer should have a transport resistance of 250 m²-sec-Pa^{1/2}/mol, about 1/6 of the measured resistance for the total membrane. There are several uncertainties in the estimate of this resistance: the substrate diffusivity and solubility values are uncertain, and there are known non-idealities of transport [18] caused by the non-negligible hydrogen concentrations (hydrogen to metal ratios about 0.3, for these experiments). Still, to a first approximation, the non-idealities cancel at these concentrations [18], and the above should be a fair estimate of the substrate permeation resistance.

A second source of transport resistance in the tubular membrane comes from the 2 μm thick palladium coats on the entrance and exit faces. If these coats were pure palladium, this would have added almost 400 m²-sec-Pa^{1/2}/mol [15] of transport resistance. It seems likely that this resistance is closer to 500 m²-sec-Pa^{1/2}/mol because permeation in palladium-5%phosphorus is likely to be slower than in pure palladium. Thus, the palladium provides more transport resistance than the substrate.

Much of rest of the transport resistance for the tubular membrane came from the gas-phase. The source flow rate for these experiments was 150 cm³/min, and the sweep flow was about 100 cm³/min. Since only hydrogen transfers through the membrane, there is a layer of methane that builds up on the upstream

membrane surface (concentration polarization), and another of high-pressure hydrogen on the downstream face. As a conservative estimate of the significance of these effects, consider the flow as laminar and axial, and broken by the presence of the swagelok connectors shown, Fig. 3. For this case, the Nussault number will be at least $1/3$, and gas-phase transfer on each side of the membrane resistance will have reduced transport by more than 35%. These estimates are conservative in that the swageloks could have increased the gas-phase resistance even further, especially at the tube ends. Given the uncertainty here, the experimental transport resistance agrees surprisingly well with the total of the resistances calculated so far. However, since transport in the gas phase is proportional to pressure, and since this effect was about $1/2$ the observed resistance, we should not expect that the overall transport rate will be proportional to driving pressure to the $1/2$ power. By deduction, the transport resistance at the palladium-niobium interface cannot be one of the largest resistances, this observation supports previous experiments [4].

Membrane durability

Coated-metal membranes do not appear to degrade from 100 hr contact with flowing methane or nitrogen at temperatures up to 450°C . This result agrees with earlier experiments [15] that showed no degradation in palladium-coated zirconium membranes that were exposed to one month of hydrogen-extraction experiments in which flowing oxygen was used as the low pressure sink for the hydrogen, i.e. "oxidative extraction." By contrast, Sawatzki and Ledoux [10] indicate that coated zirconium membranes must be annealed at 700°C or the palladium peels off. Possibly, the phosphorus contamination of our membranes increased the attachment between the palladium coat and the substrate. Without this phospho-

rus, a high-temperature anneal might have been necessary. We suspect that the phosphorus contamination decreased the membrane flux by decreasing the permeability of the palladium, and possibly by forming a barrier to hydrogen transport. Another possibility is that intermetallic interdiffusion is the source of the additional barrier to transport [11,12,19]. Based on a theoretical analysis of the rates of interdiffusion [11,12], we suggested that a palladium coat thicknesses of $1\text{ }\mu\text{m}$ would allow membranes to last 3 years or more at operating temperatures below 550°C . This analysis is supported by the observation of Sawatzki and Ledoux [10] that membranes can be annealed for several hr at 700°C without being affected adversely. Edlund has suggested that including a layer of silica between the layers of palladium and refractory metal should prevent intermetallic interdiffusion barriers from forming at high temperatures [19].

Comparison to other membranes

It is worthwhile to compare hydrogen transport through these membranes with that with other hydrogen-extraction membranes. Figure 6 compares the flux through a $3/8"$ diameter, tubular, coated niobium membrane to the flux with a commercial UBE polymeric membrane [20]. A theoretical line is shown: this is what the flux would be through this membrane if gas-phase resistance were eliminated, and if resistance in the palladium layer were reduced to $250\text{ m}^2\text{-sec-Pa}^{1/2}/\text{mol}$. The flux through the coated-niobium membrane is higher than with the commercial polymer membrane for most normal pressure differentials. Also, since these membranes are much stronger than polymer membranes, one can use larger diameter, thin walled membranes; this should reduce the pressure drop in the flowing gas as well. When compared to simple tubes of palladium and its alloys, typically $150\text{ }\mu\text{m}$ wall [1,21], the hydrogen

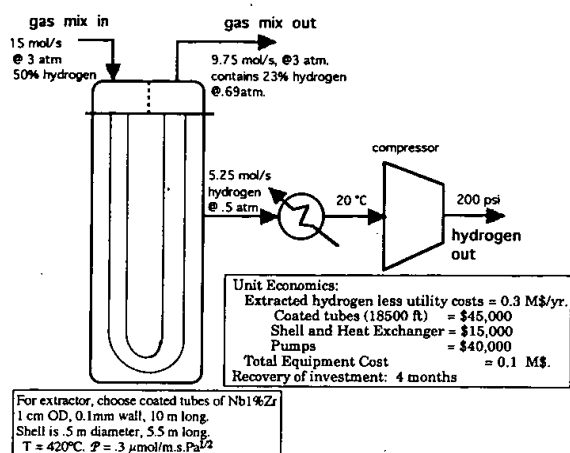


Fig. 7. Apparatus for hydrogen extraction from a 1×10^6 scf/day hydrogenation off-gas stream, with projected economics. Hydrogen value estimated as \$2.50/kg-mol.

flux with the coated membranes is higher by an order of magnitude, and the price per foot is lower. Even with current technology, the coated membranes could be effective at replacing palladium membranes in small hydrogen purification and membrane-reactor equipment (e.g. Refs. [1,16]).

It is also instructive to compare the tubular palladium-coated niobium membrane to a similar palladium-coated ceramic membrane described by Uemiya et al. [21]. The coated ceramic membrane resembles the coated niobium tube in size, shape and construction. The substrate for the coated ceramic membrane was a 1 cm OD, porous-glass tube (310 nm pores); this was electroless-coated with 13 μm of palladium. Uemiya et al. found that hydrogen selectivity was 100%, and that the flux was 0.156 mol/m²-sec (21 cm³/cm²-min) at 420°C. An analysis of the resistance can be made similarly to the above. If ΔP was 298 kPa to 102 kPa (2 kg/cm²) the transport resistance would be 1450 m²-sec-Pa^{1/2}/mol, which is identical to the resistance we measured with the coated refractory membrane. However, there are intrinsic differences. The palladium layer on the coated

ceramic probably had a transport resistance about 1300 m²-sec-Pa^{1/2}/mol, and there was an effective 150 m²-sec-Pa^{1/2}/mol caused by Knudsen diffusion in the pores. The coated ceramic had no gas-phase mass-transfer resistance since the fluxes were measured with pure hydrogen. Thus, while the total effective resistances of these membranes are identical, the intrinsic resistances are different. The flux with the coated ceramic would have been lower if a gas mixture had been used.

Uemiya et al. [21] note that the coated ceramic membranes develop pin-hole cracks when exposed to hydrogen at less than 300°C, presumably from the α - β transformation of the palladium [1,16]. Even a few pin-holes drastically reduces the membrane selectivity [21], and this strongly reduces the membranes value in reactor applications [22]. Coated refractory metals are not as susceptible to pin-holes in the palladium because the non-porous substrate blocks all but hydrogen transfer. Coated-niobium membranes swell and embrittle at temperatures below 350°C when exposed to high-pressure hydrogen, but tantalum-based membranes do not appear to be as susceptible to this problem. The coated vanadium membrane showed no sign of embrittlement.

It should be possible to increase the flux in palladium-coated metal membranes significantly by reducing the thickness of the coat and substrate, and by decreasing the gas-phase mass transfer resistance (e.g. by using a turbulent gas flow). According to eqn. (3), the flux in any metallic layer should increase with decreasing layer thickness. Since the refractory metals are much stronger than polymer, or ceramic membranes, it should be possible to make durable membranes with wall thicknesses of less than 0.1 mm (100 μm), palladium coats less than 1 μm , and diameters on the order of 1 cm. For such membranes operated in turbulent gas flow, we can predict substantially lower resistances, resulting in hydrogen fluxes in excess of 2000

scf/hr-m² for a driving force of 3 atm.

Figure 7 shows a simple design and economic analysis for metal-membrane based hydrogen recovery from a 1×10^6 scf/day hydrotreating off-stream. If the scale-up works as predicted, these membranes appear very attractive. Other applications include hydrogen recovery from cat-cracker off-gas, membrane reactor use (e.g. for enhanced an alkane dehydrogenation), purification of laboratory gas for gas chromatography, ultra-purification of hydrogen for semiconductor manufacture, and large-scale hydrogen pumping via oxidative extraction [1,12,16,23,24]. Since tantalum is currently fabricated into heat exchangers, hydrogen extractor fabrication should not involve too much additional development. It is likely that the price per square meter is comparable for all the membranes discussed [23,25].

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- 25 Early research into coated metal membranes was supported by the National Science Foundation through Grant Award No. CPE 8205021.

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(FILE 'HOME' ENTERED AT 15:23:10 ON 10 AUG 2003)

FILE 'CAPLUS' ENTERED AT 15:23:25 ON 10 AUG 2003

L1 0 S BUXBAUM AND NIOBIUM AND HYDROGEN AND MEMBRANE
L2 15 S BUXBAUM
L3 0 S L2 AND NIOBIUM

FILE 'REGISTRY, CAPLUS' ENTERED AT 15:30:25 ON 10 AUG 2003

L4 5385 S NB AND (ZR OR HF) AND (PD OR RU OR RH OR PT OR AU OR RE)
L5 2286 S L4 AND ALLOY

FILE 'CAPLUS' ENTERED AT 15:32:56 ON 10 AUG 2003

L6 13 S L5 AND MEMBRANE

=> s l6 and diffusion

464064 DIFFUSION

L7 5 L6 AND DIFFUSION

L7 ANSWER 1 OF 5 CAPLUS COPYRIGHT 2003 ACS on STN

ACCESSION NUMBER: 2003:158936 CAPLUS

DOCUMENT NUMBER: 138:387472

TITLE: Application of rare metal-noble metal membranes to the purification of hydrogen

AUTHOR(S): Chen, Shaohua; Xing, Pifeng; Chen, Wenmei

CORPORATE SOURCE: School of Chemical Engineering, Sichuan University, Chengdu, 610065, Peop. Rep. China

SOURCE: Xiyou Jinshu (2003), 27(1), 8-17

CODEN: XIJID9; ISSN: 0258-7076

PUBLISHER: Xiyou Jinshu Bianjibu

DOCUMENT TYPE: Journal; General Review

LANGUAGE: Chinese

AB A review of the advantages and disadvantages of methods to purify hydrogen isotopes to obtain ultra-high purity (99.9999%) H gas. The development and application of solid state **diffusion** membranes based on rare metal-noble metal alloys, e.g. **Pd-Ag** alloys, are discussed in detail. The merits and demerits of currently used **Pd-Ag alloy** membranes are considered. To prep. highly selective H-permeable membranes, the surface of the refractory metal used, e.g. **Zr, Nb, Ta** and **V** is modified. The requirements for a **membrane** are i.a. highly selective H-permeability, noble metal-**Pd** catalytic activity for H, and oxidn. resistance. The highly selective H-permeable membranes prepd. are able to produce ultra-high purity H gas.

IT Membranes, nonbiological

(review of application of rare metal-noble metal membranes in purifn. of hydrogen)

IT 1333-74-0P, Hydrogen, preparation

RL: PUR (Purification or recovery); PREP (Preparation)

(review of application of rare metal-noble metal membranes in purifn. of hydrogen)

IT 7440-05-3, Palladium, uses 7440-22-4, Silver, uses

RL: TEM (Technical or engineered material use); USES (Uses)

(review of application of rare metal-noble metal membranes in purifn. of hydrogen)

L7 ANSWER 2 OF 5 CAPLUS COPYRIGHT 2003 ACS on STN

ACCESSION NUMBER: 1987:109546 CAPLUS

DOCUMENT NUMBER: 106:109546

TITLE: Palladium-catalyzed oxidative **diffusion** for tritium extraction from breeder-blanket fluids at low concentrations

AUTHOR(S): Hsu, Cheazone; Buxbaum, Robert E.

CORPORATE SOURCE: Dep. Chem. Eng., Michigan State Univ., East Lansing, MI, 48824-1226, USA

SOURCE: Journal of Nuclear Materials (1986), 141-143(Pt. A), 238-43

CODEN: JNUMAM; ISSN: 0022-3115

DOCUMENT TYPE: Journal

LANGUAGE: English

AB Oxidative **diffusion** can ext. H from metal solns. at extremely low partial pressures. The H diffuses through a metal **membrane** and is oxidized to water. The oxidn. reaction produces the very low downstream pressures that drive the flux. This method is attractive because the flux can be proportional to the square-root of upstream pressure. For fusion reactors with liq. Li or Li-Pb **alloy** breeder blankets, permeation windows provide a simple, cheap T extn. method. Interdiffusion rates, sepn. flux, window size, He contents, T holdup costs, and overall costs are calcd. for membranes of Pd-coated **Zr, Nb, V, Ni** and stainless-steel. For extg. T from $^{17}\text{Li}^{83}\text{Pb}$ at 0.26 wppb, the cheapest window is V-Pd; the cost is 2.6 M\$, and the T holdup is negligible.

IT Oxidation catalysts
(palladium-coated metal, for tritium extn. from breeder blanket fluids)

IT Membranes
(palladium-coated metal, in tritium extn. from breeder blanket fluids)

IT Nuclear fusion reactors
(blankets, palladium-catalyzed oxidative **diffusion** for tritium extn. from)

IT Membranes
(**diffusion**, for tritium extn. from breeder blankets)

IT 10028-17-8P, Tritium, preparation
RL: PREP (Preparation)
(extn. of, from breeder blanket fluids using palladium-catalyzed oxidative **diffusion**)

IT 7440-62-2, Vanadium, uses and miscellaneous
RL: USES (Uses)
(membranes from palladium and, for tritium extn. from breeder blanket fluids)

IT 7440-02-0, Nickel, uses and miscellaneous 7440-03-1, Niobium, uses and miscellaneous 7440-67-7, Zirconium, uses and miscellaneous 12597-68-1, Stainless steel, uses and miscellaneous
RL: USES (Uses)
(membranes from palladium and, for tritium extn. from breeder blanket fluids)

IT 73369-65-0 7439-93-2, Lithium, uses and miscellaneous

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RL: PROC (Process)
(tritium extrn. from breeder blanket fluid of. using palladium-catalyzed
oxidative **diffusion**)

L

7 ANSWER 4 OF 5 CAPLUS COPYRIGHT 2003 ACS on STN

ACCESSION NUMBER: 1974:72526 CAPLUS

DOCUMENT NUMBER: 80:72526

TITLE: Hydrogen **diffusion** apparatus

INVENTOR(S): Eguchi, Takashi; Gotoh, Yoshiaki

PATENT ASSIGNEE(S): Japan Pure Hydrogen, Inc.

SOURCE: Jpn. Tokkyo Koho, 5 pp.

CODEN: JAXXAD

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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JP 48030233	B4	19730918	JP 1968-49679	19680716
PRIORITY APPLN. INFO.:			JP 1968-49679	19680716

AB An app. is described for prepg. high-purity H by **diffusion** through a **Pd-alloy membrane**. The H prepd. by electrolysis of H₂O is led into the app. at 500.degree.. The H is initially passed through a metal sponge (e.g., Ti, Zr, V, **Hf**, Th, Ta, Ce, La, **Nb**, etc.) sandwich between two porous sintered metal plates and then comes into contact with the **Pd alloy** in the form of thin-walled tubes open at one end. The metal sponge removes any O in the H and prevents any adverse change of the **Pd alloy** because it releases or absorbs H in proportion to the increase or decrease, resp., of the temp. With such an app. H with a dew point of -75.degree. contg. 0.1 ppm O was obtained.

IT 1333-74-0P. preparation
RL: PREP (Preparation)
(high-purity, app. for)

L7 ANSWER 5 OF 5 CAPLUS COPYRIGHT 2003 ACS on STN

ACCESSION NUMBER: 1966:428056 CAPLUS

DOCUMENT NUMBER: 65:28056

ORIGINAL REFERENCE NO.: 65:5168c-d

TITLE: Transition metal hydrides

INVENTOR(S): Oka, Akira

SOURCE: 5 pp.

DOCUMENT TYPE: Patent

LANGUAGE: Unavailable

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
FR 1410887		19650910	FR	
PRIORITY APPLN. INFO.:		JP		19631010

AB Pure H for producing the hydrides is prepd. by **diffusion** through a **Pd alloy membrane** at -70.degree. as given in U.S. 2,773,561 (CA 51, 4604b). E.g., 99.9% Ti is degassed in vacuo in a stainless steel tube at 800.degree., and then hydrogenated at 450.degree. at atm. pressure. If desired, a bed of Ti may be used for the gas purification. The TiH₂ powder may be powdered in the absence of O to aerosol dimensions, in which form it is thermally decomposable to pyrophoric Ti at 500.degree.. Similar preps. may be made from Zr, Hf, V, Nb, or Ta. **Alloy** frits may be useful for superconductors. Steel may be coated with alc. suspensions, and heat treated to give non-corrodible surfaces.

IT Transition metal hydrides
(manuf. of, and metal powder manuf. from)

IT Coating(s)
(of iron, with transition metal hydrides)

IT Conductors, electric
(super-, sintering of, hydrides in)

IT 12770-26-2, Hafnium hydride, HfH₂
(manuf. of, and Hf powder manuf. from)

IT 13981-86-7, Niobium hydride, NbH
(manuf. of, and Nb powder manuf. from)

IT 13981-95-8, Tantalum hydride, TaH
(manuf. of, and Ta powder manuf. from)

IT 7704-98-5, Titanium hydride, TiH₂
(manuf. of, and Ti powder manuf. therefrom)

IT 13966-93-3, Vanadium hydride, VH
(manuf. of, and V powder manuf. from)

IT 7704-99-6, Zirconium hydride, ZrH₂
(manuf. of, and Zr powder manuf. therefrom)

IT 7440-32-6, Titanium
(powd., manuf. from TiH₂)

IT 7440-58-6, Hafnium
(powd., manuf. of, from HfH₂)

IT 7440-62-2, Vanadium

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- (powd., manuf. of, from VH)
- IT 7440-25-7, Tantalum
 - (powder, manuf. from TaH, compression after)
- IT 7440-03-1, Niobium
 - (process metallurgy of, from niobium hydride (NbH))

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7 ANSWER 3 OF 5 CAPLUS COPYRIGHT 2003 ACS on STN

ACCESSION NUMBER: 1985:618170 CAPLUS
 DOCUMENT NUMBER: 103:218170
 TITLE: Coated **diffusion membrane** and its use
 INVENTOR(S): Harris, Jesse R.
 PATENT ASSIGNEE(S): Phillips Petroleum Co. , USA
 SOURCE: U.S., 4 pp. Cont. of U.S. Ser. No. 185,712, abandoned.
 CODEN: USXXAM
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 4536196	A	19850820	US 1982-358570	19820316
PRIORITY APPLN. INFO.:			US 1980-185712	19800910

AB In the dehydrogenation of a hydrocarbon at 800-1300.degree.F. hydrogenation takes place in a reaction zone in the presence of a **membrane** selectively permeable to H, which continuously removes H from the reaction zone by **diffusion**. The **membrane** is composed of a **Pd** or a **Pd alloy** and .ltoreq.1 metal of Group (IVB), Group (VB), and Group (VIB) metals, where the surface of the **Pd** or **Pd alloy** is coated with the 2nd metal. Suitable 2nd metals include **Zr**, **Hg**, **Ti**, **V**, **Nb**, and **Ta**, and **Ag**. Thus, a **membrane**, prepd. by plating **Ti** on a 75:25 (wt.%) **Pd-Ag alloy**, was used to sep. H from a H-C2H4 [74-85-1] mixt.

IT Petroleum refining
 (dehydrogenation, hydrogen sepn. in, permeable **membrane** for)

IT 7440-05-3, uses and miscellaneous 11122-11-5
 RL: DEV (Device component use); USES (Uses)
 (membranes contg., for sepn. of hydrogen from unsatd. hydrocarbons, in petroleum dehydrogenation)

IT 7440-03-1, uses and miscellaneous 7440-25-7, uses and miscellaneous
 7440-32-6, uses and miscellaneous 7440-58-6, uses and miscellaneous
 7440-62-2, uses and miscellaneous 7440-67-7, uses and miscellaneous
 RL: USES (Uses)
 (palladium **alloy**-based membranes contg., for sepn. of hydrogen from unsatd. hydrocarbons, in petroleum dehydrogenation)

IT 74-85-1P, preparation
 RL: PREP (Preparation)
 (prepn. of, by dehydrogenation of ethane, sepn. of hydrogen in, permeable **membrane** for)

IT 1333-74-0P, preparation
 RL: PREP (Preparation)
 (sepn. of, from unsatd. hydrocarbons, permeable **membrane** for)